

# Analysis of electron-positron momentum spectra of metallic alloys as supported by first-principles calculations

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Electron-positron momentum distributions measured by the coincidence Doppler broadening method can be used in the chemical analysis of the annihilation environment, typically a vacancy-impurity complex in a solid. In the present work we study possibilities for a quantitative analysis, i.e., for distinguishing the average numbers of different atomic species around the defect. First-principles electronic structure calculations determining self-consistently electron and positron densities and ion positions are performed for vacancy-solute complexes in Al-Cu, Al-Mg-Cu, and Al-Mg-Cu-Ag alloys. The ensuing simulated coincidence Doppler broadening spectra are compared with measured ones for defect identification. A linear fitting procedure, which uses the spectra for positrons trapped at vacancies in pure constituent metals as components, has previously been employed to find the relative percentages of different atomic species around the vacancy [A. Somoza *et al.*, Phys. Rev. B **65**, 094107 (2002)]. We test the reliability of the procedure by the help of first-principles results for vacancy-solute complexes and vacancies in constituent metals.

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## I. INTRODUCTION

In metallic alloys solute-vacancy association is one of the basic processes controlling the precipitation phenomenon. Vacancies mediate transport of solute atoms and contribute to the stability of precipitates by reducing misfit stresses between them and the matrix material.<sup>1</sup> The precipitation process is technologically important, since it improves mechanical properties of a number of light Al- and Mg-based alloys widely used in the vehicle industry.

Positron annihilation spectroscopy is a well-recognized technique for investigating metallic alloys.<sup>2,3</sup> The kinetics of precipitation after mechanical and thermal treatments can be studied by positron lifetime spectroscopy while the chemical environment of defects can be determined by Coincidence Doppler Broadening (CDB) spectroscopy. The use of CDB spectroscopy was extended to study the association of vacancies with solute atoms in metallic solid solutions only a few years ago<sup>4,5</sup> but several CDB works regarding alloys have been published since then.<sup>2,6,7,8,9,10</sup>

CDB spectroscopy suits especially well to study solute-vacancy complexes in Al alloys because, as open-volume defects, they trap effectively positrons. Moreover, typical solute atoms, such as Cu, Zn and Ag, have occupied *d* atom shells giving strong signals in CDB momentum spectra in contrast to Al. The analysis of CDB spectra is expected to give average concentrations of solute elements neighboring vacancies or vacancy-like defects at matrix-precipitate interfaces. Somoza *et al.*<sup>6</sup> suggest to fit CDB spectra with linear combinations of spectra measured for the matrix metal in the annealed state and those of elemental samples corresponding to all the constituents of the alloy after severe plastic deformation. The annealed matrix spectrum accounts for the annihilation of

free positrons in bulk whereas the deformed sample spectra take into account the effects of positron confinement at vacancies. Recently, the scheme has been revised by Ferragut<sup>11</sup> to take into account the non-saturation positron trapping by using the simultaneously measured positron lifetime spectra. Appendix shows examples of the fitting scheme in the case of Al-Cu alloy samples.

In the present work we study possibilities for quantitative analysis of solute-vacancy complexes in metallic alloys. More specifically, we choose the binary Al-Cu, ternary Al-Mg-Cu, and quaternary Al-Mg-Cu-Ag alloys and model the solute-vacancy complexes in them by first-principles electronic structure calculations. In the simulations the ion positions are determined consistently with the electron density and also with the density of the trapped positron. The CDB spectra are also measured for the as-quenched and one-minute aged Al-1.1 at. % Cu samples. The theoretical and experimental spectra are compared in order to find the most probable complexes present in the samples. The comparisons also emphasize the importance of fully relaxed ionic structures in calculating the CDB spectra.

We also study the reliability of the fitting procedure by Somoza *et al.* by comparing the first-principles results for different solute-vacancy complexes in binary, ternary, and quaternary alloys with those obtained by the linear combination of spectra calculated for vacancies in elemental deformed metals. A surprisingly good correspondence is found showing that the average numbers of solute atoms decorating the vacancy can be determined. However, in some cases this may happen with the price of modifying the fraction of trapped positrons. Moreover, the distinction between adjacent atoms in the Periodic Table, e.g. Mg and Al, may be difficult.

The present paper is structured as follows. In Sec. II we describe the defect models used in this work and in

Sec. III our computational approach. Results and discussion are presented in Sec. IV. Finally, we present our conclusions in Sec. V.

## II. MODELING

In this work we present the CDB data as ratio-difference (RD) spectra

$$\Delta(p) = \frac{\rho(p) - \rho_{\text{bulk}}(p)}{\rho_{\text{bulk}}(p)}, \quad (1)$$

where  $\rho(p)$  and  $\rho_{\text{bulk}}(p)$  are the spectra corresponding to the vacancy defect and perfect bulk systems, respectively. This presentation is convenient, because partial annihilation in the bulk state (non-saturation trapping) in the defect system does not affect the shape of the RD spectrum but only its amplitude.<sup>12</sup> Moreover, in the ratio systematic theoretical errors in momentum density intensities cancel out.<sup>13</sup> When only one type of defect traps positrons, the trapping fraction  $F$  is the multiplicative factor needed to scale the defect spectrum (corresponding to saturation trapping) to coincide the measured spectrum of the given defected system.<sup>12</sup> This fraction can be compared with the fraction obtained from positron lifetime measurements. However, usually in the case of alloys only mean lifetimes can be extracted from the experiment and therefore  $F$ , in practice, acts as a free parameter in the fitting procedure.

We start to build up the model for vacancy-solute defects in Al alloys by considering deformed Al. This is because the positron data for the alloy resembles that of deformed Al in the sense of similar trapped positron lifetimes of 210...220 ps (Ref. 14), which are clearly shorter than the positron lifetime of 235 ps for as-quenched Al (Ref. 12). In the previous work<sup>12</sup> we modeled a vacancy in deformed Al by moving the nearest-neighbor atoms of the vacancy inward and keeping the more distant atoms in their ideal Al lattice positions. The inward relaxation mimics the effects of strain due to dislocations with which vacancies are associated. In this work we want to calculate from first-principles the positions of the Al and solute atoms and therefore the strain is taken into account by reducing the Al lattice constant. We choose the strain to reproduce the experimental positron lifetime value of  $225 \pm 1$  ps for trapped positrons (Ref. 12). The strain needed is 4% with respect to the experimental lattice constant of 4.05 Å, resulting in a lattice constant of 3.89 Å. Also the Doppler spectra for the vacancy in this strained Al is in a reasonable agreement with the experimental data for deformed Al (Ref. 12). Namely, the predicted curve has the correct shape and the scaling needed corresponds to the trapping fraction of 48% which is comparable to the value of 64% deduced from the positron lifetime measurements. Apart from using the empirically determined lattice constant we model the geometries of the vacancy-solute complexes from first principles. This

means that the ionic structures of complexes are determined by minimizing the Hellman-Feynman forces due to the electronic structure and the localized positron state.<sup>13</sup>

Here we want to remark that the determination of the amount of strain is actually based not only on the agreement of the theoretical and experimental positron lifetimes for the deformed Al; Also for the unstrained case our lifetimes agree well with the experimental ones (See Table I). Namely, for the bulk we get the theoretical lifetime of 165 ps in good agreement with the experimental values of 153, 158, and 163 ps (Refs. 15,16 and 17) and our theoretical lifetime of 248 ps for the vacancy is consistent with the experimental ones of 235...248 ps (Refs. 12 and 17). For the vacancy-Cu complexes in Al the experimental lifetimes are around 210 ps (Ref. 14) and our modeling, as will be discussed below in more detail, gives typically 210...220 ps.

In our tests for the fitting procedure by Somoza *et al.* we need also the CDB spectra corresponding to vacancies in deformed Cu, Mg, and Ag. Similarly to the Al case their modeling is performed by using slightly reduced lattice constants. They are given in Table I along with the resulting positron lifetimes. The lifetimes are also compared with the measured ones. For Cu and Ag the absolute values are typically too low, but the important relative differences between the vacancy and bulk lifetimes agree well with experiment. In the case of Mg, theory predicts a larger lifetime difference than the measured one.

Figure 1 shows the RD spectra relative to bulk Al calculated using the first-principles methods for vacancies in strained Al, Mg, Cu, and Ag metals. At high momenta the Al and Mg RD spectra are rather similar, reflecting the reduction of annihilation with similar electron cores. The Al spectrum has a peak around  $9 \times 10^{-3} m_0c$  due to positron confinement.<sup>12</sup> In the Mg RD spectrum there is a maximum at low momenta reflecting the rather low electron density (and long positron lifetime) at the vacancy. In the Cu RD spectrum the high level at high momenta is due to annihilation with Cu 3d electrons whereas in the case of Ag the peak at  $10 \times 10^{-3} m_0c$  originates from Ag 4d electrons. The difference between the Cu and Ag RD spectra reflects the difference in the localization of the 3d and 4d electrons. The latter are more delocalized because 4d wave functions have to be orthogonal against 3d wave functions. The spectra in Fig. 1 are in good agreement with the experimental data presented in Ref. 26 and with those used in the experimental fitting procedure.<sup>11</sup>

## III. COMPUTATIONAL METHOD

We model defects in the face-centered (fcc) Al, Cu, and Ag lattices using a cubic supercell of 32 atomic sites. For the hexagonal Mg we use an orthorhombic supercell with 48 atomic sites. Valence electron densities are

TABLE I: Theoretical  $\tau_{\text{theor}}$  and experimental  $\tau_{\text{exp}}$  positron lifetimes for elemental bulk metals and vacancies in them. Also the lattice parameters,  $a$  for the face-centered cubic and the  $c/a$  ratios for the hexagonal close-packed structures, are shown. The non-strained lattice parameters are experimental values at room temperature.<sup>18</sup>

System	$a$ (Å)	$c/a$	$\tau_{\text{theor}}$ (ps)	$\tau_{\text{exp}}$ (ps)
Al bulk, no strain	4.05		165	153 <sup>a</sup> , 158 <sup>b</sup> , 163 <sup>c</sup>
Al vacancy			249	235 <sup>d</sup> , 236 <sup>a</sup> , 248 <sup>c</sup>
Al bulk, strained	3.89		149	
Al vacancy, strained			226	225 <sup>e</sup> , 240 <sup>f</sup>
Cu bulk, no strain	3.61		103	109 <sup>a</sup> , 112 <sup>b</sup> , 119 <sup>g</sup>
Cu vacancy			175	168 <sup>a</sup> , 170 <sup>h</sup> , 180 <sup>i</sup>
Cu bulk, strained	3.52		95	
Cu vacancy, strained			160	170 <sup>h</sup> , 178 <sup>e</sup>
Mg bulk, no strain	3.21	1.62	230	219 <sup>j</sup> , 225 <sup>k</sup>
Mg bulk, strained	3.05	1.62	217	
Mg vacancy, strained			285	244 <sup>e</sup>
Ag bulk, no strain	4.09		123	131 <sup>l</sup> , 131 <sup>a</sup>
Ag vacancy			196	207 <sup>a</sup>
Ag bulk, strained	3.97		111	
Ag vacancy, strained			189	196 <sup>e</sup>

<sup>a</sup>Reference 15

<sup>b</sup>Reference 16

<sup>c</sup>Reference 17

<sup>d</sup>Reference 12

<sup>e</sup>Reference 19

<sup>f</sup>Reference 20

<sup>g</sup>Reference 21

<sup>h</sup>Reference 22

<sup>i</sup>Reference 23

<sup>j</sup>Reference 11

<sup>k</sup>Reference 24

<sup>l</sup>Reference 25

computed self-consistently in the framework of the local-density approximation (LDA) of the density-functional theory; the computations are carried out by employing the plane-wave code VASP<sup>27,28,29</sup> with the projector augmented-wave (PAW) method<sup>30</sup> to account for the valence electron-ion core interaction. The first Brillouin zone of the superlattice is sampled using the  $8 \times 8 \times 8$  Monkhorst-Pack  $\mathbf{k}$ -point mesh.<sup>31</sup> A plane-wave cutoff of 342 eV is used when calculating the pseudo-valence wavefunctions, in which the rapid oscillations near to ion cores are smeared off. The ionic structures of the vacancy-type defects are relaxed taking into account also the forces on ions due to the localized positron.<sup>13</sup> Thereby electron and positron densities and ion positions depend on each other and they are solved in a self-consistent fashion. The PAW method enables also the post-construction of all-electron valence wavefunctions which we use to calculate accurately electron momentum densities.<sup>13,32</sup> The cut-off equivalent to the momentum of the electron-positron pair of  $70 \times 10^{-3} m_0 c$  is used when expanding all-electron valence wavefunctions in plane waves.

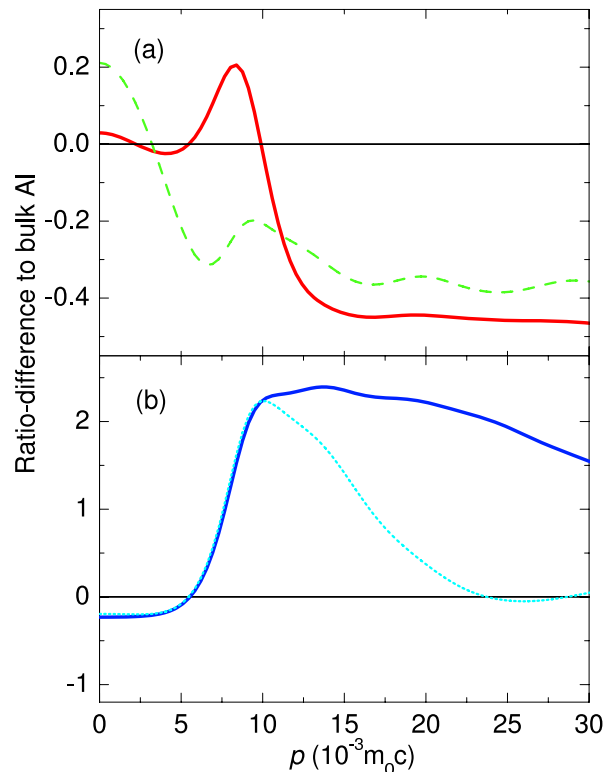


FIG. 1: (Color online) Calculated CDB RD spectra for vacancies in elemental strained metals. (a) The solid (red) line shows the result for the vacancy in strained Al and the dashed (green) line for the vacancy in strained Mg. (b) The solid (dark blue) line is the result for a vacancy in strained Cu and the dotted (light blue) line for the vacancy in strained Ag.

Using the PAW total charge density including the free atom core electrons the positron potential is constructed within the LDA (Ref. 33) for electron-positron correlation effects. Then the lowest-energy positron state is calculated on a three-dimensional real-space point grid.<sup>13</sup> The so-called “conventional scheme”, in which the localized positron density does not affect directly the average electron density, is used to describe trapped positrons. The annihilation rates of self-consistent all-electron valence states and those of the atomic core electron states are calculated within the LDA (Ref. 33) for the electron enhancement at the positron. These partial annihilation rates are used as weighting factors when calculating momentum densities of annihilating electron-positron pairs within the so-called state-dependent enhancement scheme.<sup>34,35</sup> For Al matrix systems the momentum distributions corresponding to valence electrons are obtained by the three-dimensional Fourier transformation on a cubic grid with the spacing of  $0.67 \times 10^{-3} m_0 c$  and those for the core electrons on a dense radial grid using parameterized forms of the positron wavefunction.<sup>34</sup> The momentum densities for bulk Cu, Ag, and Mg and vacancies in them are calculated with accuracies similar to that for Al matrix. The ensuing three-dimensional momentum distributions are integrated over planes per-

pendicular to the [100] direction and convoluted with a Gaussian function with the full width at half maximum (FWHM) of  $3.6 \times 10^{-3} m_0c$  in order to simulate experimental CDB spectra. In the case of asymmetric defects we average over all possible orientations of the defect. For a complete description of the computational method see Ref. 13. Calloni *et al.*<sup>12</sup> have previously used the same methodology (without the first-principles determination of the ionic relaxation) to study clean monovacancies in strained Al.

## IV. RESULTS AND DISCUSSION

### A. Ionic structures of vacancy-Cu complexes in the Al-Cu alloy and positron lifetime results

We have simulated vacancy-Cu complexes in the Al-Cu alloys by varying the number of Cu atoms, nearest neighbors to the vacancy, between 1 and 12. The resulting relaxed geometries and corresponding lifetimes are described in Table II. Up to 4 Cu atoms it is reasonable to assume that the Cu atoms are on the same [100] plane around the Al vacancy maximizing the Cu-Cu distances. This is because according to Atomic Probe Field Ion Microscopy (APFIM) experiments Cu tends to form platelets perpendicular to the  $\langle 100 \rangle$  direction<sup>1,14,36</sup> and also because according to our calculated total energies these configurations are favored in contrast to more dense Cu clusters. However, as listed in Table II, in addition to these planar configurations we have considered 3 Cu atoms as nearest neighbors to each other and 4 Cu atoms in a tetragonal configuration.

According to Table II the larger the number of Cu atoms around the vacancy, the stronger the outward relaxation of the Cu atoms and the inward relaxation of the Al atoms. For less than 4 Cu atoms also the Al atoms tend to relax outward, but much less than the Cu atoms. The relatively long positron lifetime in the case of 12 Cu atoms is related to the strong outward relaxation, which increases the vacancy size compared with the other defects. The strong tendency of the Cu atoms to relax outward from the ideal Al lattice sites is in accordance with the Effective Medium Theory by Jacobsen *et al.*<sup>37</sup> which indicates that in metallic environments Cu atoms seek to a much higher electron density than Al atoms. The theory explains also why, according to our calculations, the change of the Cu atom configuration for a fixed number of Cu atoms does not alter significantly the open volume of the defect and the positron lifetime.

### B. Comparing the experimental Al-Cu spectra with calculations for model systems

We proceed by analyzing experimental CDB data for Al-Cu alloys using the previously described calculations for realistic model defects. Different simulated RD spec-

TABLE II: Relaxations and positron lifetimes for vacancy-Cu complexes in the Al-Cu alloy. In the case of 4 Cu atoms, the planar and tetragonal configurations are considered. The ranges of relaxations are given for both Al and Cu nearest neighbors to the vacancy. The relaxations are relative to the ideal lattice positions and given in % of the bond length in the strained Al. A positive (negative) value denotes outward (inward) relaxation.

No. of Cu atoms	Relaxation, Al (%)	Relaxation, Cu (%)	Lifetime (ps)
0	+1.6	–	226
1	+0.5 ... +1.5	+7.3	223
2	+0.3 ... +0.8	+6.9	221
3 <sup>a</sup>	–0.6 ... +1.1	+5.6 ... +6.2	218
3 <sup>b</sup>	+1.1	+5.6 ... +6.2	218
4 <sup>a</sup>	–0.9	+5.9	216
4 <sup>c</sup>	–2.7 ... +0.4	+5.4 ... +7.8	217
6	–3.3 ... –2.1	+5.9 ... +6.8	213
8	–5.7	+5.5	210
10	–9.9	+3.0 ... +11.0	223
12	–	+7.4	235

<sup>a</sup>On the [100] plane

<sup>b</sup>Nearest neighbors

<sup>c</sup>Tetragonal

tra are scaled separately so that the least squares method gives the best fit with those measured for the as-quenched and 1-min aged Al–1.1 at. % Cu samples. The experimental procedure for obtaining these spectra is explained in Appendix. Thus, we assume first that a single defect geometry can represent the whole defect distribution in the sample in an average manner. As explained above, the scaling means the fitting of the fraction  $F$  of positrons trapped at defects. Figure 2(a) shows the results for the as-quenched sample and simulated spectra with 2, 3, and 4 Cu atoms. Data for momenta up to  $15 \times 10^{-3} m_0c$  are included in the fitting. The best fit is obtained with 3 Cu atoms with the scaling corresponding to the trapping fraction of 62%. The fits with 2 and 4 Cu atoms are clearly worse. Figure 3(d) below shows that taking the linear combination of the 2 and 4 Cu atom spectra with equal weights we obtain a fit which practically coincides with the 3 Cu atom spectrum. Even the scaling needed remains the same. We can therefore conclude that the sample contains a distribution of vacancies with 3 Cu nearest neighbors on the average.

The above analysis using the first-principles-simulated RD curves agrees well with the analysis based on the linear combination of measured spectra for bulk Al and for deformed Al and Cu (see Appendix). The fitting gives the Cu contribution of  $23 \pm 1.5\%$ , i.e., there are roughly 3 Cu atoms among the 12 nearest neighbors of the vacancy on the average. The trapping fraction is found to be  $73 \pm 1\%$  which is slightly larger than the estimate based on the theoretical spectrum.

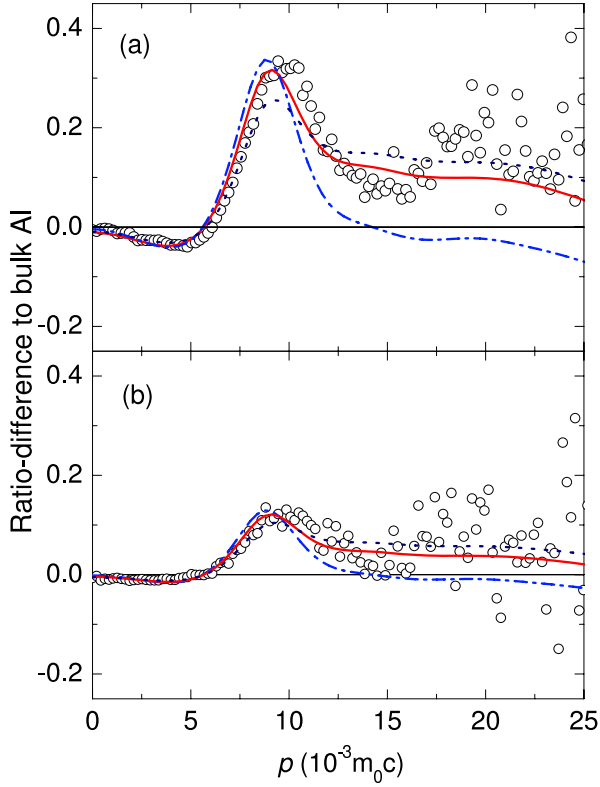


FIG. 2: (Color online) Experimental CDB spectrum ( $\circ$ ) (RD to bulk Al) of (a) an as-quenched Al-1.1 at. % Cu sample, and (b) the same sample aged 1 min at 150 °C. The dash-dotted (blue), solid (red), and dotted (black) lines show the best one-component fits obtained for vacancy-Cu defects with 2, 3, and 4 Cu atoms, respectively.

In the case of the 1-min aged sample the experimental data points [Fig. 2(b)] are quite scattered because of the lower vacancy concentration and smaller trapping fraction. This complicates the fitting. However, as Fig. 2(b) shows we get a reasonable fit also in this case when having 3 or 4 Cu atoms next to the vacancy. These fits result in trapping fractions of 24% or 17%, respectively. These numbers should be contrasted with the experimental analysis of Appendix indicating the Cu concentration of  $33 \pm 5\%$ , i.e. about 4 Cu atoms around the vacancy and the trapping fraction of  $18 \pm 1\%$ . However, because of the very scattered experimental data and low trapping fraction, it is difficult to draw accurate conclusions about the number of Cu atoms around the vacancy.

Now we want to get an idea about the importance of different ingredients of our first-principles calculations on the simulated CDB RD spectra. Our reference system is the Al vacancy in the strained Al lattice decorated with 3 Cu atoms. Due to the good agreement with the experimental result shown in Fig. 2(a) this suits well as a representative test case. Figure 3(a) shows that ignoring the lattice relaxation relative to the ideal lattice positions increases the intensity at high momenta and decreases the relative intensity of the peak at around  $p = 9 \times 10^{-3} m_0 c$ .

This change reflects the tendency of the Cu atoms to relax strongly outward (see Table II). The reduction of the number of Cu atoms to 2 would improve the agreement with experiment but still the shape is worse than that of the fully relaxed 3-Cu-atom case. The importance of using the strained Al lattice is emphasized in Figure 3(b). Ignoring the strain increases the intensity at low momenta indicating a too large open volume and a too long positron lifetime. The negative values at high momenta can be healed by increasing the number of Cu atoms to 4 but this affects by worsening the relative intensity of the peak. Figure 3(c) shows that 3 Cu atoms nearest neighbors to each other result in a large intensity increase at high momenta with respect to the 3 Cu atoms on the same [100] plane. This is because the dense Cu cluster creates open volume attracting the positron density and resulting in an increased annihilation with Cu 3d electrons. However, as discussed above, the planar configuration is favored against the dense one due to its lower calculated total energy and also due to the experimental findings.

### C. Linear combinations of elemental CDB spectra: theory vs theory

The most important goal of the present work is to test the reliability of the linear combination method adopted in the experimental data analysis (see Appendix). For example, the RD spectrum  $\Delta(p)$  for a vacancy-Cu complex in the Al-Cu alloy is fitted with the function

$$\begin{aligned} \Delta^{\text{Fit}}(p) &= F[C_{\text{Al}}\Delta_{\text{Al}}^{\text{Vac}}(p) + C_{\text{Cu}}\Delta_{\text{Cu}}^{\text{Vac}}(p)] \\ &= F\left[\frac{N_{\text{Al}}}{12}\Delta_{\text{Al}}^{\text{Vac}}(p) + \frac{N_{\text{Cu}}}{12}\Delta_{\text{Cu}}^{\text{Vac}}(p)\right], \end{aligned} \quad (2)$$

where  $\Delta_{\text{Al}}^{\text{Vac}}(p)$  and  $\Delta_{\text{Cu}}^{\text{Vac}}(p)$  are the RD spectra for vacancies in strained (i.e., deformed) Al and Cu, respectively.  $F$  is the fraction of trapped positrons and  $N_{\text{Al}}$  and  $N_{\text{Cu}}$  are the numbers of Al and Cu nearest neighbors to the vacancy, respectively. The Al and Cu concentrations around the vacancy fulfill the constraint  $C_{\text{Al}} + C_{\text{Cu}} = 1$ , so that there are only two free fitting parameters, e.g.,  $F$  and  $C_{\text{Cu}}$ . Actually,  $F$  should be ideally equal to unity, but we will keep it as a fitting parameter in order to test the idea of the general fitting procedure. Figure 1 shows the theoretical elemental RD spectra we use in our fitting.

Instead of the experimental Al-Cu alloy data we use here the RD spectra calculated from our first-principles results for Al vacancies decorated with Cu atoms and fit them using the similarly calculated RD spectra for vacancies in strained Al and Cu. Figure 4 shows the simulated RD curves for 2, 4, 8 and 12 Cu atoms as the nearest neighbors to the vacancy. The linear combinations obtained with the least squares method and their Al and Cu vacancy components are also shown. The momentum range of  $0 \dots 15 \times 10^{-3} m_0 c$  is included in the fitting. As in

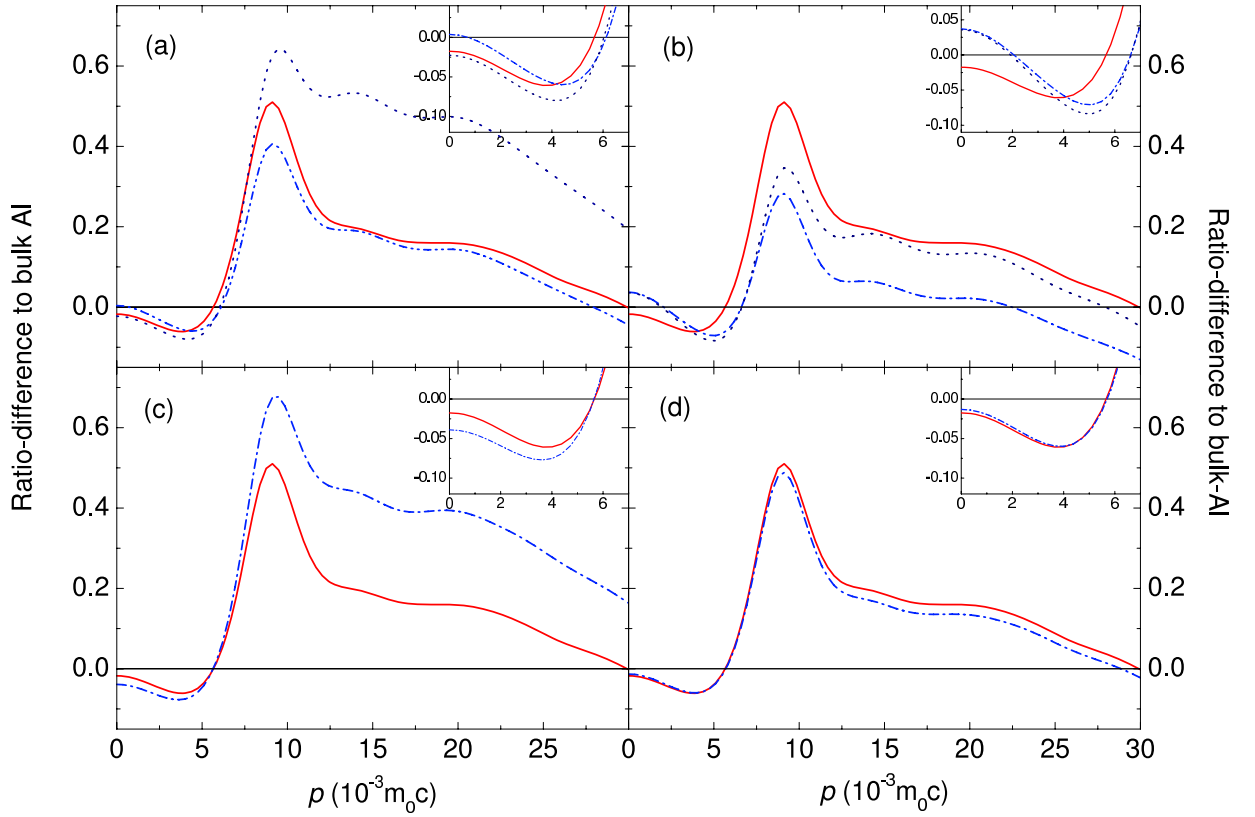


FIG. 3: (Color online) Influence of different approximations on the first-principles results for Al vacancies decorated with Cu atoms. In all panels the solid (red) line shows the RD spectrum obtained for the Al vacancy surrounded by 3 Cu atoms on the [100] plane in the strained Al lattice including ionic relaxation due to the electronic structure and the localized positron state. (a) The (dark blue) dash-dotted and the (blue) dotted lines show the results corresponding to ideal (no relaxation) ion positions and for 2 and 3 Cu atoms, respectively. (b) The (dark blue) dash-dotted and the (blue) dotted lines correspond to the Al lattice without strain and to 3 and 4 Cu atoms, respectively. (c) The (dark blue) dash-dotted curve shows the result for 3 Cu atoms nearest neighbors to each other. (d) The (dark blue) dash-dotted curve corresponds to the fit using the linear combination of RD spectra for 2 and 4 Cu atoms with equal weights.

the purely experimental analysis the fits reproduce successfully the original curves. The decompositions show that the peak around  $8 \times 10^{-3} m_0 c$  in the RD spectrum is due to the Al vacancy component and Cu 3d derived electronic states are responsible for the raise of the intensity at high momenta. At the low-momentum region of  $0 \dots \sim 7 \times 10^{-3} m_0 c$  the agreement between the simulated RD curve and the linear combination worsens with increasing number of Cu atoms surrounding the Al vacancy. This is due to the fact that the electron density at the vacancy in Cu is larger than that at the Al vacancy surrounded by Cu atoms.

More quantitatively, the fitting parameters  $F$  and  $C_{Cu}$  are given in Table III. The fitting seems to underestimate the Cu concentration consistently by around 10%. This rather good accuracy is obtained by the help of the reduction of the trapping fraction from its nominal value of unity. When the number of Cu atoms increases from 1 to 12,  $F$  decreases rather linearly from a value slightly less than unity to around 0.7. The reduced trapping fraction substitutes the annihilation with Cu by annihilation with bulk Al. This compensation is needed because the use of

the Cu vacancy data would otherwise lead to too strong annihilation with Cu atoms due to the fact that the Cu lattice constant is smaller than that for Al. The reduced trapping fraction decreases also the contribution  $FC_{Al}$  of the Al-vacancy RD spectrum. This decrease is compensated by the increase of the ratio  $C_{Al}/C_{Cu}$ . But the effect of this “secondary” compensation is not strong and it decreases with the decreasing number of Cu atoms so that the ratio  $C_{Al}/C_{Cu}$  remains close to the correct one. Thus, the Cu concentration is estimated to be only 10% too small.

#### D. Vacancy-solute complexes in Al-Cu-Mg and Al-Cu-Mg-Ag alloys

Next we want to investigate possibilities for quantitative analysis of vacancy-solute complexes when there are more than one type of solute atoms. As examples we choose complexes in the technologically important ternary Al-Cu-Mg and quaternary Al-Cu-Mg-Ag alloys. The Al matrix around the defect complex is described by

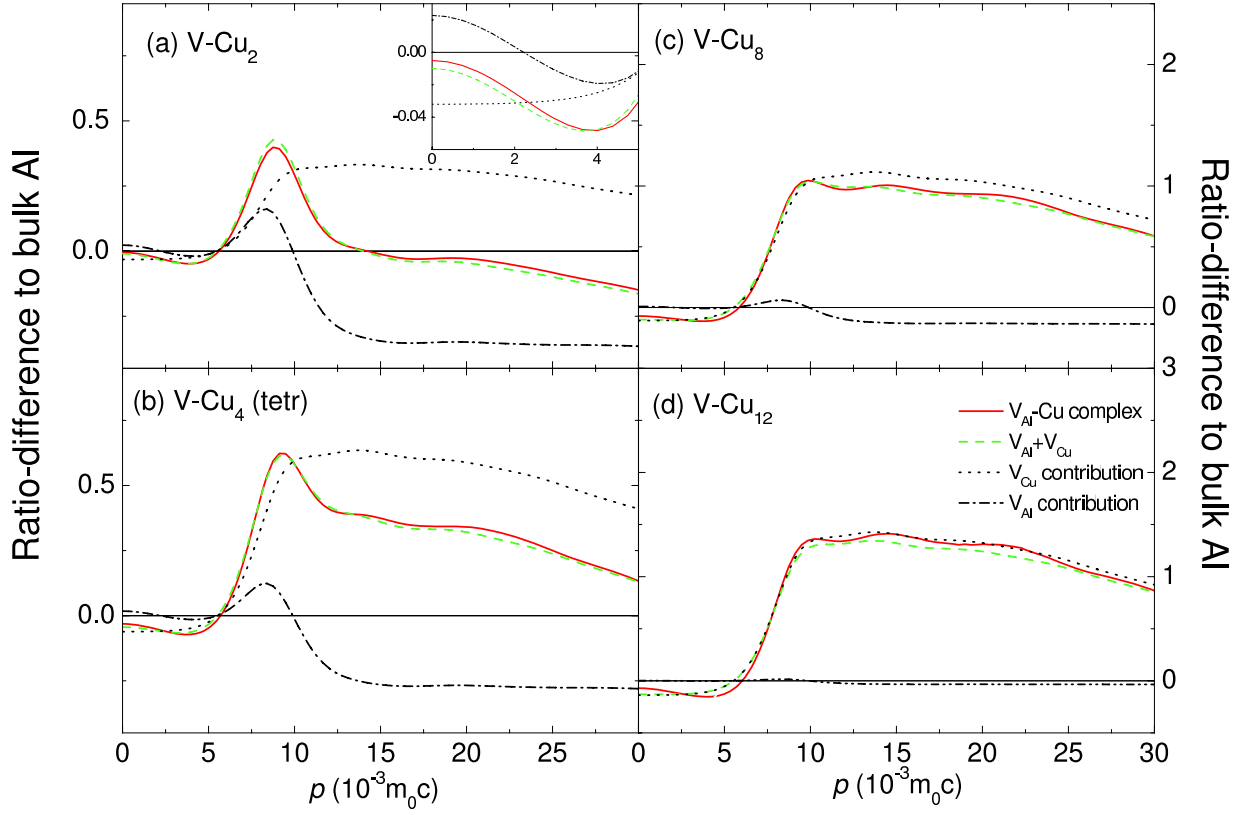


FIG. 4: (Color online) CDB RD spectra for vacancy-Cu complexes in Al-Cu alloys with (a) 2, (b) 4, (c) 8, and (d) 12 nearest neighbor Cu atoms. The tetragonal configuration is used in the case of 4 Cu atoms. The solid (red) curves give the results of the first-principles calculations. The dashed (green) curves are the linear combinations [Eq. (2)] of the RD spectra calculated for vacancies in strained Al and Cu. The dash-dotted and dotted curves show the Al and Cu contributions, respectively. The inset in (a) shows the low-momentum region magnified.

TABLE III: Fitting the RD spectra calculated from the first-principles results for vacancy-Cu complexes in the Al-Cu alloy with the linear combination of calculated RD spectra for vacancies in strained Al and Cu. The fitting parameters, i.e., the number  $N_{\text{Cu}}$  of Cu atoms around the Al-vacancy and the fraction of trapped positrons  $F$  are defined in Eq. (2).

No. of Cu atoms in complex	$N_{\text{Cu}}$	$F$
1	1.00	0.967
2	1.80	0.924
3 <sup>a</sup>	2.71	0.898
3 <sup>b</sup>	3.84	0.912
4 <sup>a</sup>	3.49	0.842
4 <sup>c</sup>	3.67	0.868
6	5.54	0.811
8	7.38	0.758
10	9.05	0.762
12	10.66	0.671

<sup>a</sup>On [100] plane

<sup>b</sup>Nearest neighbors

<sup>c</sup>Tetragonal

the strained Al lattice as above for the Al-Cu alloy. The ionic and electronic structures and the trapped positron density are calculated with the first-principles scheme.

Figure 5(a) shows the RD spectra of vacancy-Cu-Mg complexes when there are 2 Cu and 0, 1, and 2 Mg atoms as nearest neighbors to the vacancy. All the solute atoms are on the same [100] plane with the two Cu atoms along a  $\langle 110 \rangle$  direction. According to Fig. 1(b) one would expect that the primary effect of the increasing number of neighboring Mg atoms on the shape of the defect RD spectrum would be to linearly increase its intensity at low momenta. However, this is not the case. In Fig. 5(a) the effect of Mg at low momenta is negligible. At high momenta where the annihilation with Cu 3d derived states and Al and Mg core states dominates in the defect spectrum the effect of Mg is to increase positron annihilation with these states. First of all, Mg has a larger Wigner-Seitz radius than Al. This means that the open volume at the vacancy decreases with the increasing number of Mg atoms. The relaxation of Mg atoms in these systems is about  $-1.3 \dots -1.2\%$  (minus sign denotes inward relaxation). The positron lifetime increase per Mg atom added is 2 ps. The effect of the decreased vacancy volume on the CDB RD spectrum is to increase core annihilation and



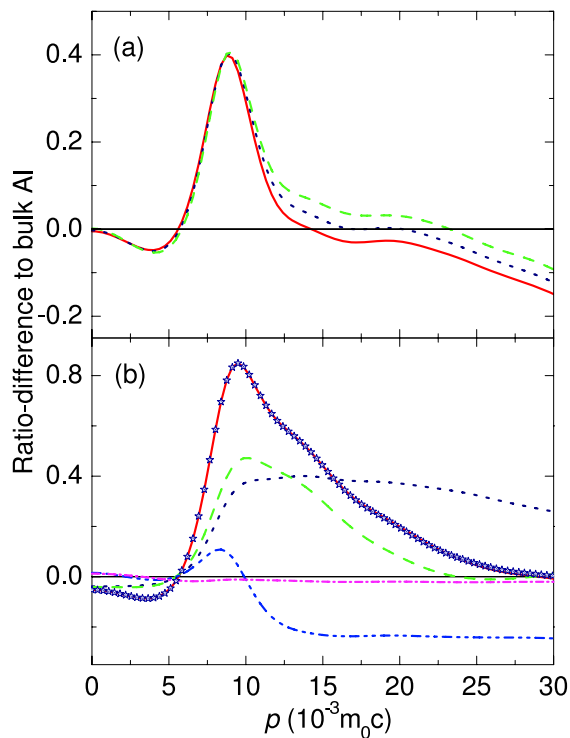


FIG. 5: (Color online) (a) CDB RD spectra for vacancy-Cu-Mg complexes in Al-Cu-Mg alloys with 2 Cu and 0, 1, and 2 Mg atoms denoted by solid (red), dotted (dark blue) and dashed (green) lines, respectively. (b) CDB RD spectrum for a vacancy surrounded by 2 Cu, 2 Mg, and 2 Ag atoms and the best linear-combination fit denoted by a solid (red) line and (blue) stars, respectively. The components of the fit, corresponding to vacancies in strained Al, Cu, Mg, and Ag, are shown by (blue) dash-double dotted line, (dark blue) dashed line, (pink) dash-dotted line, and (green) long-dotted lines, respectively.

decrease annihilation with low-momentum valence electrons at the vacancy. On the other hand, substituting Al by Mg decreases the electron density at the vacancy which in turn increases the value of the RD spectrum at low momenta. This effect, however, is not strong enough to raise the peak at low momenta. This fact is also seen in results of simulations in which there is only Al and Mg around the vacancy.

The possibility of quantitative identification of Mg at the vacancy-solute complexes is studied in Table IV which shows the analysis results of the RD spectra calculated for several vacancy-Cu-Mg complexes. Up to 4 solute atoms they are on the same [100] plane. A general trend is that Cu atoms tend to relax strongly outward from the center of the vacancy, up to  $\sim 10\%$  of the Al bond length, whereas Mg atoms tend to relax slightly smaller amounts inward. The different behaviors reflect the trends in the Wigner-Seitz radii. The fitting with the spectra for vacancies in elemental strained metals is performed in the momentum range of  $0 \dots 15 \times 10^{-3} m_0 c$ . According to Table IV the trapping fractions are closer

to unity than in the case of vacancy-Cu complexes in Table III. This is because Cu has a smaller and Mg a larger Wigner-Seitz radius than Al so that their effects tend to compensate each other. The analysis gives rather faithfully the correct number of Cu atoms. But the number of Mg atoms is clearly underestimated. This is because the Mg component in the fit, i.e., the RD spectrum for a vacancy in strained Mg has a rather strong peak at low momenta due to the large Wigner-Seitz radius and the low electron density. In the denser Al lattice Mg does not decrease the electron density to the portion deduced on the basis of the effect of the vacancy in Mg. Moreover, the effect on the RD spectrum at low momenta is not necessary a linear function of the number of Mg atoms as discussed above.

Table IV shows also results for vacancy-Cu-Mg-Ag complexes. In these systems the fitting procedure which is now extended up to  $17 \times 10^{-3} m_0 c$  reproduces the correct trapping fraction extremely well. Also  $N_{\text{Cu}}$  and  $N_{\text{Ag}}$  are described with reasonable accuracy. Ag can be separated because due to the  $4d$  electrons its RD spectrum has in contrast to those of Mg and Al a strong intensity at high momenta but on the other hand the Ag  $4d$  contribution decays much faster than the Cu  $3d$  contribution towards high momenta [see Fig. 1(b)]. For this reason, when analyzing systems with Ag it is crucial to extend the momentum fitting region at least up to  $17 \times 10^{-3} m_0 c$  in order to be able to differentiate between Ag and Cu. Again, the Mg content is underestimated but the sum  $N_{\text{Al}} + N_{\text{Mg}}$  is described well. Figure 5(b) shows as a typical example the spectrum and its decomposition for the vacancy complex with 2 Cu, 2 Mg, and 2 Ag atoms.

## V. SUMMARY AND CONCLUSIONS

We have performed first-principles calculations for electronic structures, positron states, and ion positions at solute-vacancy complexes in metallic alloys Al-Cu, Al-Mg-Cu, and Al-Mg-Cu-Ag. The ensuing positron annihilation characteristics, positron lifetimes and momentum distributions of annihilating electron-positron pairs have been calculated. Since the electron and positron densities as well as the ion positions depend on each others they have to be determined in a self-consistent fashion. We have shown that this step is required in order to obtain annihilation characteristics consistent with the experimental ones.

Calculated ratio-difference curves of the Doppler broadening spectra are compared with measured ones in order to identify quantitatively the vacancy-solute defects, i.e., to determine the average numbers of different solute atoms around the vacancies. An experimental spectrum can be interpreted in terms of a spectrum calculated for a certain defect configuration or by a linear combination of spectra for two or more defect configurations.

By the help of the first-principles results for vacancy-



TABLE IV: Fitting the RD spectra calculated from the first-principles results for vacancy-Cu-Mg and vacancy-Cu-Mg-Ag complexes in the Al-Cu-Mg and Al-Cu-Mg-Ag alloys with the linear combination of calculated RD spectra for vacancies in strained Al, Cu, Mg, and Ag. The fitting is done by generalizing Eq. (2) to four components  $N_{\text{Al}}$ ,  $N_{\text{Cu}}$ ,  $N_{\text{Mg}}$ , and  $N_{\text{Ag}}$  giving the number of Al, Cu, Mg and Ag atoms around the vacancy, respectively. The fitting parameter  $F$  is related to the fraction of trapped positrons.

No. of Cu atoms	No. of Mg atoms	No. of Ag atoms	$N_{\text{Cu}}$	$N_{\text{Mg}}$	$N_{\text{Ag}}$	$F$
1	1		1.07	0.32		0.954
2	1		1.94	0.58		0.932
2	2		2.09	0.99		0.919
2	4		2.37	1.69		0.895
2	6		2.60	2.51		0.900
3	1		2.78	0.89		0.912
3 <sup>a</sup>	1		2.87	0.66		0.906
3	3		3.16	1.40		0.894
4	4		4.10	2.19		0.868
5	2		4.79	1.52		0.882
2	2	2	2.08	0.71	2.63	0.963
2	4	2	2.60	1.40	1.77	0.980
4	2	2	3.66	1.12	2.35	0.975
3	1	1	3.10	0.53	0.81	0.994
3 <sup>a</sup>	1	1	3.10	0.74	0.58	1.01
3	1	2	2.97	0.51	1.96	1.00
3 <sup>a</sup>	1	2	2.93	0.55	2.05	1.01

<sup>a</sup>Different configuration of the nearest-neighbor solute atoms

solute complexes and vacancies in constituent metals we have tested the linear fitting procedure suggested by Somoza *et al.* to find the percentages of different atomic species around the vacancies. With the Al-Cu, Al-Mg-Cu, and Al-Mg-Cu-Ag alloys as test cases we have shown that the linear combination can resolve the average number of solute atoms whose electronic structures differ clearly from those of the matrix and other solute atoms (such as Cu and Ag in our tests). Typically, an accuracy better than 0.5 ... 1.0 atoms from the 12 nearest neighbors can be achieved. However, adjacent atoms of the Periodic Table having similar core electron structures (such as Mg and Al) cannot be distinguished.

In our test cases the most important momentum region for the linear combination fits is above  $\sim 7 \times 10^{-3} m_0c$ . In this region the behavior of the electron wave functions near the ion cores is important leading to distinction of the different atomic species. The lower momenta are dominated by free-electron type behavior which depends mainly on the average valence electron density seen by the positron. The introduction of solute atoms does not introduce changes like new covalent bonds which would affect the above division to free-electron and atomic-specific regions. However, in order to mimic this division

in linear combination fits in a reasonable manner it is important to use the vacancy spectra, not the bulk spectra of solute metals as components.

The linear fitting procedure works well also due to compensating effects affecting the positron annihilation rates with different ion cores. The rates depend on open space seen by the positron and this may differ between the matrix and solute metal lattices. Compensation may occur when there are two or more different types of solute atoms around the vacancy. Compensation may also occur by underestimating or overestimating the fraction of trapped positrons if the fraction is kept as a free parameter in the fit. Therefore comparing the fitted trapping fraction with that obtained by using the positron lifetime measurements is a valuable tool to check the consistency of the linear fitting procedure.

## APPENDIX: DETAILS OF THE EXPERIMENTS AND THE EXPERIMENTAL FITTING PROCEDURE

The experimental data presented below refer to two pairs of samples of a well-homogenized laboratory alloy, obtained by melting commercially pure elements. The nominal composition of the alloy was Al-1.1 at. % Cu. All samples were solution treated by holding at 525°C for 1 h, then water quenched at room temperature. One pair of samples was immediately mounted in the standard sandwich configuration with a <sup>22</sup>Na positron source (about  $2 \times 10^5$  Bq) sealed between Kapton foils and brought at liquid nitrogen temperature within less than a minute since quenching. The second pair was aged in oil bath for 1 min at 150°C, then quenched again at room temperature, mounted with the positron source and cooled as described for the other pair. All lifetime and CDB measurements were taken simultaneously at liquid nitrogen temperature; set-ups and procedures were already described in Ref. 12. The momentum resolution was  $3.69 \times 10^{-3} m_0c$  (FWHM). The time resolution of the lifetime apparatus was 250 ps (FWHM).

The analysis of the lifetime spectrum was carried out by means of the Positronfit program<sup>38</sup> in a single component after subtraction of 12.5% source component. The CDB empirical analysis was performed by applying a modified version of the linear combination procedure suggested by Somoza *et al.*<sup>6</sup>

In the present version, the CDB spectrum  $\rho$  was fitted with a revised version of a linear combination (see Ref. 11) of three reference spectra,  $\rho_{\text{Al}}^{\text{bulk}}$ ,  $\rho_{\text{Al}}^v$ ,  $\rho_{\text{Cu}}^v$ , measured, respectively for: (a) bulk annealed Al (no positron trapping); (b) deformed Al (100% positron trapping, after correction for the contribution of free positrons); (c) deformed Cu (100% positron trapping, after correction for the contribution of free positrons). The linear combination can be written in the form

$$\rho = (1 - F)\rho_{\text{Al}}^{\text{bulk}} + F(C_{\text{Al}}\rho_{\text{Al}}^v + C_{\text{Cu}}\rho_{\text{Cu}}^v), \quad (\text{A.1})$$

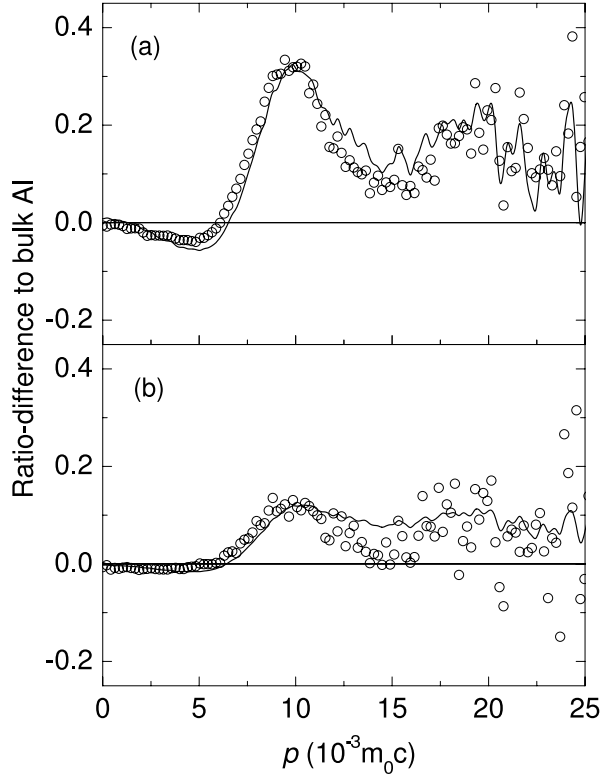


FIG. 6: Results of CDB measurements (markers) for (a) Al-1.1 at. % Cu alloy measured after quenching and (b) after 1 min aging at 150°C. The solid lines show the empirical fitting curves.

TABLE V: Empirical fitting coefficients  $F$ ,  $C_{Al}$  and  $C_{Cu}$  and the mean positron lifetimes  $\tau$  for the Al-1.1 at. % Cu alloy after quenching and after 1 min aging at 150°C.

Sample	$F$ (%)	$C_{Al}$ (%)	$C_{Cu}$ (%)	$\tau$ (ps)
As quenched	$73 \pm 1$	$77 \pm 1.5$	$23 \pm 1.5$	$196 \pm 1$
Aged 1 min at 150°C	$18 \pm 1$	$67 \pm 5$	$33 \pm 5$	$169 \pm 1$

where  $F$  is the proposed estimate of the positron fraction trapped at vacancy-solute clusters and  $C_{Al}$ ,  $C_{Cu}$  are the proposed estimates of the fractional atomic concentrations in contact with the vacancy.

The same experimental data as in Fig. 2 and the empirical fitting curve [Eq. (A.1)] are shown in Fig. 6 versus the modulus of the momentum component. The numerical results of the CDB analysis and the mean positron lifetimes are reported in Table V.

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